Chapter 1

Introduction

1.1 The Marangoni effect

In the beginning...

This thesis is concerned with the influence of the Marangoni effect on mass transfer across a liquid-gas interface. The phenomenon of liquid flowing along an interface from places with low surface tension to places with a higher surface tension is named after the Italian physicist Carlo Giuseppe Matteo Marangoni (1840-1925). Marangoni studied the conditions for spreading of one liquid on the other in, among other places, the largest basin of the Tuileries gardens in Paris. He found that a liquid A spreads on a liquid B when the sum of the interfacial tension and the surface tension of A is lower than the surface tension of B. He was the first to report on this phenomenon in a brochure [1] and made his research more widely available six years later, in 1871 [2], on account of his fear that publications by the Belgian Gustave van der Mensbrugghe [3] and the German Franz Lüdtge [4] would render his priority on this subject unacknowledged.

A more detailed historical account on the spreading phenomenon can be found in a paper by Ross and Becher [5]. However, the spreading phenomenon is only one aspect of the Marangoni effect. When gradients in surface tension arise due to concentration differences within one fluid, flow arises as well, and this phenomenon was first outlined qualitatively by James Thomson (1822-1892). Thomson, the older brother of Lord Kelvin, explained the tears found in a glass of wine or any other strong alcoholic liquor, in terms of surface tension gradients [6]. Therefore, the Marangoni effect is sometimes referred to as the Thomson effect (e.g. [7]).

The term “Marangoni effect” is also used frequently for a phenomenon that, rather than inducing movement at the interface, retards interfacial motion. Interfaces often contain traces of surface active substances that reduce the surface tension. In general, surface tension lowering solutes adsorb preferentially in the interface (Gibbs adsorption). The longer the characteristic time for a solute to redistribute itself between the interface and the bulk of the liquid, the more surface active the solute is (see for example the characteristic times presented by Bakker et al. [8]). When, for any reason, an interface expands locally, these surface active solutes are swept outward with the movement, creating a gradient in their concentration. This concentration gradient implies a surface tension gradient which acts opposite to the movement. The interfacial movement is therefore damped. This effect has been referred to as Gibbs elasticity, the Marangoni effect, and, more appropriately, as the Plateau-Marangoni-Gibbs

effect [9]. In this thesis, the latter term is used to refer to this effect. A historical treatment of both Marangoni effects is provided by Scriven and Sternling [9].

In observing, but not explaining, one of the described effects, both Marangoni and Thomson were far outdated by other authors. In 1686, Heyde observed dancing camphor on olive oil (referred to in [7] and [10]), and Varley (1836) observed curious motions in evaporating drops under a microscope [11]. Gaius Plinius Secundus (Pliny the Elder) observed the calming of the sea as a result of the spreading of oil on the water already in AD 77 [12]. And even longer ago, the bible refers to the phenomenon of tearing wine in Proverbs XXII.31 [13]: “Look not thou upon the wine when it is red, when it giveth its colour in the cup, when it glideth down smoothly”.

1.2 This thesis

In this introductory chapter, a background is presented to the work described in the following chapters. This thesis describes work on two separate issues: the enhancement of mass transfer by Marangoni convection in gas-liquid systems (chapters 2-4), and the occurrence of Marangoni convection during protein crystallisation (chapter 5).

In section 1.3, the circumstances are defined under which Marangoni flow occurs. This involves the subject of interfacial instability, and work on stability analysis is therefore reviewed. Instability analysis predicts that Marangoni flow can occur during the desorption of acetone from water into air. For this thesis, the latter system has been chosen as a model system to study the evolution of Marangoni flow. In chapter 2, experiments are discussed that are intended to study flow and concentration patterns as a result of Marangoni convection in several geometries (V-shaped containers). Why these experiments were performed in a microgravity environment is explained in section 1.4. As microgravity experiments on Marangoni convection have already been performed by the Department of Chemical Engineering of the University of Groningen since 1985, section 1.4 also presents the history leading up to the experiments described in chapter 2. In chapter 3, the flow and concentration distribution in two of these containers are modelled numerically.

The research outlined in chapters 2 and 3 was motivated by the fact that Marangoni convection can enhance mass transfer, a subject of interest to chemical engineers. In section 1.5, a literature review is presented on this subject, with the emphasis on gas-liquid systems. Some references pertaining to mass transfer in liquid-liquid systems, and the enhancement of heat transfer by Marangoni convection, are also discussed for the sake of completeness. From this literature, it is evident that Marangoni convection both influences the mass transfer coefficient and the mass transfer interfacial area. It was the intention of this thesis work to use the microgravity experiments to explain and predict the influence of the Marangoni effect on the mass transfer coefficient. Therefore, the numerical model used in chapter 3 to predict flow and concentration patterns is used in chapter 4 to study the influence of various parameters (Schmidt numbers, mass transfer phase resistance ratio, Marangoni number) on the mass

transfer in gas-liquid systems. These findings are discussed and compared to some of the literature results already presented in chapter 1.5.

In chapter 5, the possibility of Marangoni convection occurring during the crystallisation of proteins is discussed. In this chapter, a microgravity experiment is described that was intended to study possible Marangoni effects in a hanging drop protein crystalliser. Furthermore, a theoretical section is presented that gives an order of magnitude analysis on some of the issues pertaining to the Marangoni effect during protein crystallisation. Chapter 5 is a separate part of this thesis in the sense that the chapter is self-contained. The information in this chapter is provided for use by both protein crystallisation and fluid dynamics researchers, and therefore a background section on both protein crystallisation and the Marangoni effect is presented. Some of the information supplied in this introductory chapter is therefore repeated in chapter 5.

Finally, in the epilogue, the conclusions of the work described in this thesis and some ideas on future research topics are discussed.

1.3 Interfacial instability.

The Marangoni effect can occur in a liquid-gas and in a liquid-liquid system. It can be the result of concentration and/or temperature gradients. In the case of concentration gradients, the effect is called the solutal Marangoni effect. Concentration gradients in a liquid can be the direct result of mass transfer between phases, but can also be the indirect result of buoyancy or another type of convection, forced flow, heat transfer or temperature gradients in general. When temperature gradients are responsible for the Marangoni effect, the effect is frequently called thermocapillarity. Temperature gradients can be the result of heat transfer processes as well as mass transfer processes (involving enthalpy changes) or any type of natural or forced flow.

Electric and magnetic fields can also influence flow at an interface by their influence on the surface tension, although this is rarely labelled Marangoni convection. Electric fields can initiate and interact with a non-uniformity of electric conductivity and dielectric constant. Numerous papers are devoted to this electrocapillarity and to the interaction of electric [e.g. 14, 15, 16, 17, 18] and magnetic fields [e.g. 18, 19] and Marangoni and Rayleigh convection. For example, research effort has been devoted to the reduction of thermocapillarity during crystallisation from the melt in microgravity, using magnetic fields [19]. Strong non-uniform electric fields have been used to induce the electrocapillary-related spraying effect or electrohydrodynamic effect, resulting in strongly enhanced mass or heat transfer [20, 21, 22].

This thesis focuses on solutal Marangoni convection. Two different kinds of Marangoni convection can be distinguished, micro- and macroconvection [8].

Marangoni flow is labelled macroconvection when the gradient in interfacial tension is imposed on the system by an asymmetry. The circulation of candle wax in the pit of a candle, due to the temperature gradient imposed by the burning wick, and the tears in a glass of brandy

are examples of macroconvection. Macroconvection can be the result of a geometrical asymmetry or local sources or sinks of heat or mass in the interface. Other examples include mass transfer in a wetted wall column resulting in a concentration gradient parallel to the falling film [23], the so-called Marangoni drying by contacting a thin film of water with a vapour of organic liquid [24, 25], contacting an interface with a single point surface tension sink [26, 27, 28, 29], mass transfer through a system with a meniscus [30], deformation of a meniscus by a vertical temperature gradient [31], the thickening of a liquid layer on a solid drawn out of a liquid, the so-called Marangoni coating [32], and a series of examples listed by Berg in his early review on interfacial phenomena in fluid phase separation processes [33].

Microconvection, on the other hand, is flow which originates from random disturbances in the temperature or concentration field. For these random disturbances to amplify, the system needs to be unstable. An example of an unstable system is the system that is studied intensively in chapter 2 and 3 of this thesis, the acetone/water/air system with acetone evaporating from the liquid to air. Consider a water film containing acetone from which acetone is evaporating uniformly. The interfacial concentration of acetone is equal along the entire interface. It is possible that, due to some minor disturbance, the evaporation at a certain spot at the interface is reduced. Locally, the concentration of acetone increases somewhat. This effects a reduction of the surface tension. Due to the created surface tension gradient, liquid starts to flow away from the spot and is replaced by liquid from the bulk, which is even richer in acetone. So, the disturbance is amplified, and roll cells form in the liquid. In this analysis, one also has to take the air phase into account. In the air phase, the roll cells try to stop the flow, as they transport air with a low acetone concentration to the disturbed spot. Which transport process wins, or, in other words, whether the system is unstable or not, depends on, among other things, the ratio of kinematic viscosities and the ratio of diffusivities in both phases.

A formal answer to the question of instability is provided by a linear stability analysis. Sternling and Scriven published the key paper on linear stability analysis and solutal Marangoni flow in 1959 [34]. Their paper dealt with a system of two semi-infinite (X-direction) phases, in which a solute was transferred from one phase to the other. They assumed a linear, stationary concentration profile without flow as an initial situation. The flow was mathematically triggered by seeking a solution for the stream function ψ of the form:

$$\psi = \varphi(X)\, e^{i\alpha Y}\, e^{\beta t} \qquad (1)$$

In this equation, Y is the co-ordinate parallel to the interface, α the wave number of the disturbance, β the growth constant and t is time. The growth constant consists of a real and an imaginary part. If $\beta < 0$, the disturbance is damped. If $\beta > 0$, the system is stationary unstable when the imaginary part equals zero, or oscillatory unstable when the imaginary part is not equal to zero. Equation (1) was substituted in the governing equations to obtain a set of characteristic equations. By solving these equations, Sternling and Scriven were able to derive criteria for instability as a function of the ratio of kinematic viscosities, the ratio of diffusivities, the sign of the dependence of surface tension on concentration, the direction of mass transfer, and a function f in which both ratios, the distribution coefficient, the composite interfacial viscosity, the wavelength at neutral stability and the dynamic viscosities (μ) appear. From their

predictions, the water/acetone/air system described above is stationary unstable with acetone transferring to the air and oscillatory unstable when acetone is transferring from the air.

Whether a disturbance actually starts to grow in an unstable regime depends on the magnitudes of the various physical constants and whether the wavelength λ (= $2\pi/\alpha$) of the disturbance is small enough. Numerous papers have been devoted to neutral stability analyses, in which a critical Marangoni number as a function of the critical wavelength is searched for. The key paper in this field was published by Pearson in 1958 [35]. This paper deals with heat transfer induced thermocapillarity in one semi-infinite phase (the Benard case), while the second phase is represented in the linear stability analysis by a Biot type equation. The Marangoni number is frequently expressed as:

$$Ma = \frac{\left(-\frac{\partial\gamma}{\partial c}\right)c_0 H}{\mu D} \qquad (2)$$

In this equation ($\partial\gamma/\partial c$) is the dependence of surface tension on concentration, c_0 a characteristic concentration, H a characteristic length and D the diffusivity of the solute in the phase of interest. This Marangoni number expresses a ratio of a characteristic diffusion time and a characteristic time for Marangoni driven flow. The larger the Marangoni number, the larger the growth factor β. Below a critical value of the Marangoni number no α can be found for which $\beta > 0$. Various different Marangoni numbers appear in the literature, which makes comparison difficult. Marangoni numbers are also sometimes expressed as a ratio of surface tension forces and viscous drag. In other papers, a characteristic concentration gradient is incorporated in the Marangoni number. In this thesis, equation (2) is used. However, depending on the system, other expressions may be preferred. Semkov and Kolev have published a survey of Marangoni numbers used in mass transfer applications [36].

Since the publications of Pearson, and Sternling and Scriven, numerous variations on the same topic have been published. Abundant experimental work has been done to understand the interfacial instabilities and to verify Sternling and Scriven's analysis [37, 38]. Especially the work of Linde and co-workers should be quoted [39, 40, 41, 42, 43, 44, 45, 46]. Linde demonstrated the oscillatory behaviour of the absorption of acetone in water from air [42]. Some experimental work on liquid-liquid systems also has demonstrated inconsistencies between model and theory [47]. Various optical techniques have been used to study the interfacial instability qualitatively, such as Schlieren optics [8, 30, 41, 42, 48, 49, 50, 51], interferometry [52], and holographic interferometry [53, 54].

Sternling and Scriven extended Pearson's analysis to include the effect of mean surface tension and interfacial viscosity [55]. They also demonstrated that in steady cellular convection driven by surface tension, liquid flows up beneath depressions and flows down beneath elevations of the free surface. Pearson's analysis was further extended to spherical [56, 57, 58, 59, 60], cylindrical [61] and rectangular geometries, with [62] and without rigid side walls [63]. A similar analysis for gas absorption was presented by Rabinovich and Struchenko [64]. The influence of buoyancy on the onset of Marangoni convection was studied by Nield [65] and others [66, 67, 68, 69]. The influence of Gibbs absorption of the solute on the critical

Marangoni number was incorporated in a study by Brian [70]. Instead of using a linear (concentration) profile as the undisturbed situation (film theory), Brian and Ross subsequently used the penetration theory in their analysis [71]. Dupont et al. also used a non-linear profile (in this case a temperature profile) in their analysis and compared it successfully to a microgravity experiment [72]. Others included the influence of insoluble surface active agents at the interface [73], of which Berg and Acrivos were the first [74]. They demonstrated that even a very thin layer of insoluble surfactant can increase the critical Marangoni number thousand-fold. The influence of the Plateau-Marangoni-Gibbs effect on the stability of falling liquid films was investigated by Ji and Setterwall [75]. The same authors investigated linear instability during absorption in a LiBr water jet containing surfactants [76]. The addition of for example octanol to a LiBr absorption refrigeration system increases the destabilising effect of the water absorption, but stabilises the system as a result of adsorption to the interface. Also, the evaporation of octanol plays a role in the stability analysis.

According to the phase rule, no solutal Marangoni effect can exist in a binary liquid-liquid system. Sawistowski et al. observed strong interfacial movements in such systems nevertheless [51]. These instabilities were driven by temperature variations resulting from the release or the absorption of solution heat. Ortiz and Sawistowski studied the linear stability of such systems [77]. In their case, mass transfer only takes place in one of the phases and the system is unstable when the heat of solution and the rate of change of interfacial tension with temperature are of opposite sign. Evaluation of their stability criteria for some experimental systems resulted in good agreement [78]. Later, they were also confirmed in microgravity experiments [79].

Linde et al. studied the case of heat sinks or sources at an interface (as for example with the evaporation of a pure liquid) and found heat sinks to be destabilising and heat sources to be stabilising [39]. Berg et al. also demonstrated thermocapillarity for evaporating pure liquids by performing experiments with and without contamination. Only the convection patterns observed for thicker layers were sustained when the surface was contaminated [48]. A linear instability study by Aharon and Shaw for binary evaporating droplets in dry air shows that thermocapillary effects can be stabilising and solutal effects can be destabilising for alcohol-water mixtures. They derived a critical radius beyond which an evaporating droplet is unstable [80]. Ho and Chang performed an instability analysis for doubly-diffusive Marangoni problems (simultaneous heat and mass transfer) on a film of liquid bound between a solid and a gas phase [81]. Again linear (stationary) profiles were assumed for the undisturbed case.

Warmuzinski and co-workers incorporated the effect of chemical reaction [82, 83, 84], and also provided experimental evidence. Also Rabinovich included chemical reaction [85]. Warmuzinski also treated the simultaneous transfer of two solutes [86]. A first non-linear stability analysis for solutal Marangoni convection was carried out by Bragard, Slavtchev and Lebon [87]. Non-linear interaction between long-scale waves (when surface deformation is important) and short-scale waves (those occurring as a result of Marangoni convective patterns) was studied by Golovin et al. [88]. Interfacial instabilities in systems with surfactants have been discussed by Sørensen [89, 90]. Linear stability analysis with simultaneous

experimental evidence was provided by Dupont et al. [72]. Numerous other variations on the subject of stability analysis have been published [91, 92, 93, 94, 95, 96, 97, 98, 99, 100].

Bifurcation analysis was used to determine the preferential number and the form of roll cells in a stationary unstable situation [101]. The famous experiments of Benard [102, 103], who demonstrated roll cells in a liquid layer heated from below, and Koschmieder and Prahl [104, 105] were modelled in three-dimensional geometries with different aspect ratios by Dijkstra [106, 107]. Golovin et al. studied pattern selection in the case of non-linear interaction between long-scale and short scale instabilities [108] in a gas-liquid system, as a follow-up on their earlier study [88]. Mancini and Maza experimentally studied oscillatory patterns in the Benard case with and without lateral sidewalls for high Prandtl number fluids [109]. Other authors experimentally studied patterns in a liquid layer locally heated on its free surface (reversed Benard case) and found more and more complex (chaotic) patterns with increasing Marangoni number [110]. More papers on the question of pattern selection have been published [111].

Later, the linear stability analysis has been used as a prelude to predict transient flow development [112]. Stationary flow patterns in a double-diffusive system were calculated by Bergman [113]. The influence of contamination in double diffusive spherical systems was investigated by Lyell and Carpenter [114]. Others predicted stability and flow development in rectangular slots, with [115, 116] and without [117, 118] the presence of surfactants. An up to date text book on the subject of convective instabilities was recently published by Simanovskii and Nepomnyashchy [119].

A separate way to treat Marangoni convection has been based on the work of Lucassen [120, 121] on longitudinal waves. In his theory, an interface is an elastic membrane that can propagate longitudinal waves (as well as transversal waves). Theoretical work based on dispersion relations for these longitudinal waves has been performed by Gouda en Joos, in order to predict linear stability, and they arrived to more or less the same conclusions as Sternling and Scriven [122]. Their work was improved by Hennenberg et al. [123, 124, 125, 126]. Other authors continued to work on longitudinal waves, sometimes referred to as Marangoni waves or Lucassen-Marangoni waves [127].

Several authors have pursued the subject of so-called solitary waves [128, 129, 130, 131]. Under conditions which can lead to oscillatory instabilities (heating a liquid layer from the air side, absorbing acetone in water), single capillary waves sustained by Marangoni convection can originate. These waves can collide with each other and with walls and show those non-linear features which are characteristic of solitonic behaviour [132]. Wave patterns found by Weh and Linde [130] under these conditions strongly resemble those found by Favre et al. [110], although the experimental conditions are slightly different.

Reviews on the Marangoni effect and other surface tension driven phenomena have been published by for example Kenning ([133], 1968), Levich and Krylov ([134], 1969), Velarde and Castillo ([135], 1982), Davis ([136], 1987), Myshkis et al. ([137], 1987), Legros et al.

([138], 1987) and Rabinovich ([139], 1992). A text book on interfacial rheology, including interfacial mass transport has been published by Edwards, Brenner and Wasan [12].

1.4 Marangoni versus Rayleigh convection; the use of a microgravity experiment

Buoyancy, or Rayleigh convection, can occur at the same time as Marangoni convection. The same concentration and temperature gradients that are responsible for surface tension gradients, also create density gradients. The intensity of the density driven convection is characterised by the Rayleigh number. This Rayleigh number is expressed as:

$$Ra = \frac{\left(-\frac{\partial \rho}{\partial c}\right) c_0 g H^3}{\mu D} \qquad (3)$$

In this equation, ρ is the density, and g is the gravity acceleration. This number is similar to the Marangoni number (equation (2)), but the effect of the characteristic dimension is much larger. Usually, the Rayleigh effect dominates the flow in liquid layers with dimensions larger than one centimetre. The Marangoni effect usually dominates when the characteristic dimension is smaller than one millimetre. For chemical engineers, the layers of 1 mm are more relevant as these layers are more often encountered in mass transfer equipment. However, it is practically impossible to study the flow pattern in such thin layers, not even with the help of a sophisticated Laser-Doppler anemometer [140]. Furthermore, no practical system exists in which $(\partial\gamma / \partial c) / (\partial\rho / \partial c)$ is that large that the Marangoni effect overshadows buoyancy in thicker layers. Therefore, the only way to study Marangoni flows separately from buoyancy in 1 cm layers, is by experiments in a reduced gravity environment.

In chapter 2 of this thesis, experiments with the unstable acetone/water/air system in a microgravity environment are described. In the past, other microgravity experiments with this system have been performed by the department of chemical engineering of the University of Groningen. Lichtenbelt, Dijkstra en Drinkenburg studied the flow development in a rectangular container on board of the Spacelab D1 flight in 1986 [141, 142]. Later, Lichtenbelt and Drinkenburg, followed by Hoefsloot and Janssen, performed similar experiments in a ventilated bubble configuration on board of the Maser-1 [142] and Maser-2 sounding rocket flights and during parabolic flights [143].

To the surprise of the investigators, no roll cells were observed initially in the D1-flight, despite predictions from linear stability analysis [63]. However, when the payload specialist retracted a little fluid and a concave meniscus was obtained, Marangoni convection was observed along the entire interface. Later these observations were explained by the assumption that surface active substances had partly polluted the interface, thereby increasing the critical Marangoni number above the experimental one. Upon creation of a concave meniscus, a macroscopic concentration gradient was created, since the edges of the meniscus were relatively poor in acetone compared to the liquid in the centre. (Similar phenomena were

observed earlier by Kayser and Berg [144]). The experiment was simulated numerically by introducing a gradient in the effective Biot number across the interface [142].

The D1-experiment raised the question whether the curvature of the interface was important in determining the instability criteria. Therefore, air bubbles with various curvature were investigated in sounding rocket experiments. In the experiments, a container was filled with an acetone-in-water solution. Air was blown in between two tips to form a spherical air bubble in the liquid. The air was continuously circulated and cleaned. By varying the distance between the tips, bubbles of various sizes (curvature) were created. In all of the experiments convection was observed and no definite conclusions on the influence of curvature could be drawn. However, the experiments with the air bubbles of various sizes gave different flow patterns. This proved to be the result of varying concentrations along the interface as a consequence of the flow pattern of air within the bubble, whereby the variation depended on the bubble size [143]. Numerical simulations confirmed this view, while other analyses showed that the influence of curvature on the onset of Marangoni convection is negligible, considering the experimental Marangoni numbers. Again, the experiments proved that it was important to differentiate between micro- and macroconvection. New experiments were therefore defined in which a varying curvature of the interface was used to create geometries that were susceptible to either micro- or macroconvection. The geometry that was chosen was the V-shaped container and preliminary experiments were performed by Hoefsloot et al. [145]. The final experiments are presented in chapter 2 of this thesis.

Numerous other experiments have been performed in microgravity to study thermocapillarity [e.g. 72, 146, 147, 148] or solutal Marangoni convection. Some of these microgravity experiments have been conceived for the same reasons as described above: to avoid Rayleigh convection in order to study the Marangoni effect separately from the Rayleigh effect. Another line of microgravity experiments involving Marangoni effects originates from the desire to produce perfect crystals. With some types of crystal growth one has to avoid all types of convection in order to grow the desired crystals. A microgravity environment can substantially reduce buoyancy, but in the presence of a liquid-liquid or gas-liquid interface, Marangoni flows do not cease to exist. Abundant microgravity experiments were designed to obtain a better understanding of the influence of Marangoni convection on crystal growth. For example, Marangoni flow in floating zones (liquid bridges), used for growing semiconductor crystals, was studied extensively, both experimentally and theoretically [e.g. 149, 150, 151, 152, 153, 154]. In chapter 5 of this thesis, the influence of Marangoni convection on the crystallisation of biological macromolecules from solution is discussed [155].

In microgravity, drops and bubbles move under the influence of a temperature gradient as a result of the Marangoni effect. When surface or interfacial tension decreases with temperature, the particle moves from cold to hot. This thermocapillary drop and bubble migration has been studied intensively by several authors [156, 157, 158, 159, 160]. A survey on this subject of relevance to material processing and manufacturing has been published by Wozniak, Siekmann and Srulijes [161], and later by Velarde [162].

Theoretical work by Nield on the interaction between Marangoni and Rayleigh convection indicated that the Rayleigh and the Marangoni effect reinforce each other [65]. Other theoretical work on combined Rayleigh and Marangoni convection was published by Wagner, Friedrich, and Narayanan [163], Dijkstra [101], Platten and Villers [164, 165], Bauer [166], and Napolitano, Viviani and Savino [167]. Experimental work on combined Rayleigh and Marangoni effects was performed by Berg and Morig [30], Berg, Boudart and Acrivos [48], Pantalonii, Bailleux, Salan and Velarde [68], Berg and Haselberger [168], Szymczyk [169], and Homsy and co-workers [170, 171].

1.5 The influence of the Marangoni effect on mass transfer processes.

Liquid gas systems

The work described in chapters 2 to 4 of this thesis was initiated by the contention that Marangoni convection can not only be caused by mass transfer, but that it can in turn also enhance this mass transfer. Actually, there are several mechanisms by which the Marangoni effect (or the Plateau-Marangoni-Gibbs effect) can influence mass transfer. Marangoni flows close to the interface increase the transport of matter to and from the interface. The Marangoni convection therefore increases the mass transfer coefficient with respect to pure diffusive mass transfer. Furthermore, the Marangoni effect can also influence the shape and size of the mass transfer interfacial area. The basic paper on the significance of the Marangoni effect for mass transfer applications was published in 1958 by Zuiderweg and Harmens [172]. Their paper dealt with the influence of surface tension gradients on the interfacial area in supported and unsupported distillation equipment. They classified the systems under investigation in three categories. Positive systems were defined as those systems in which the reflux increases in surface tension; negative systems as those systems in which the reflux decreases in surface tension and neutral systems as those systems in which the components of the distilled liquid had no appreciable surface tension difference or a very small relative volatility. In more general terms [140], a positive system can be defined as a system in which the surface tension increases due to mass transfer, a negative system as a system in which the surface tension decreases due to mass transfer and a neutral system as a system in which the surface tension remains essentially constant during mass transfer.

Zuiderweg and Harmens distinguished between unsupported interfacial area equipment (sieve trays) and supported interfacial area equipment (packed columns). They found that the separation efficiency increased for positive systems in unsupported equipment and decreased for negative systems in supported equipment, both with respect to the separation efficiency of neutral systems. For negative systems in unsupported and positive systems in supported equipment, almost no influence on the separation efficiency was found. This can be explained by considering film stability in both systems. In a thin film, variations in thickness are always present. The thinner the film, the closer the interfacial concentration approaches the equilibrium concentration. For positive systems, this means that the thinner parts of the film

exhibit an increased surface tension. Surface tension forces then pull liquid to these thinner places, making the film stable. For negative systems, on the other hand, a thinner film implies a smaller surface tension. The Marangoni effect then acts to remove even more liquid from these thinner places, and the film breaks up into rivulets. The interfacial area in supported equipment is therefore reduced in negative systems. In unsupported equipment, the tendency of positive systems to stabilise films (rather than drops) increases the interfacial area, up to the formation of foams. (This is a positive effect only up to the point of flooding, of course. Flooding as a result of Marangoni foams is occasionally found in industry [173].) Zuiderweg and Harmens further concluded that the rate of mass transfer in positive systems could be more than twice as high as the mass transfer in negative systems. The effect would be larger, the larger the driving force and the larger the difference in surface tension between the pure components. Moreover, the effect would be larger in the laboratory than in industrial equipment.

The paper of Zuiderweg and Harmens has been followed by a host of other papers on packed and sieve tray columns [174, 175, 176, 177]. Correlations were sought to relate the Marangoni effect to an in- or decrease in mass transfer as a function of driving force and surface tension differences between components. Reviews on this subject were published by Berg [33] and Sawistowski [178]. Hovestreijdt examined the influence of the Marangoni effect on bubble formation during boiling of binary mixtures [179]. He found a correlation between the maximum heat flux at the transition from nucleate boiling to unstable film boiling and the stabilisation index (as defined in formula (7) below). For large sieve trays, various prediction methods for point efficiencies exist. Dribika and Biddulph demonstrated that in systems in which the Marangoni effect is operative, none of these methods gives accurate predictions [180].

For sieve trays, it was found that a negative system could in some cases actually promote mass transfer [181, 182, 183]. Vapour blowing through the liquid on a sieve tray entrains droplets. The size of these droplets is determined by the ease with which a thin filament of liquid connecting a small droplet with the bulk of the liquid breaks up. In a negative system the filament breaks up more easily, by the same mechanism as described above. In a negative system, the droplets are smaller and the total interfacial area is therefore larger than in a positive system, provided no foaming occurs. The considerations above only apply for tray columns in which the vapour velocity is large enough to operate in the spray regime rather than in the foam regime.

The Plateau-Marangoni-Gibbs effect was also studied on sieve trays. Surfactants added in low concentration may promote foaming, because they increase film stability by the mechanism discussed in the beginning of this chapter [184, 185]. The foaming of soap solutions is an example of this phenomenon. For negative systems, the addition of small amounts of surfactants may increase the efficiency of sieve plates up to the levels of positive systems [186]. A related subject is research for anti-foaming agents in which the Plateau-Marangoni-Gibbs and the spreading phenomenon also play a role [184, 185, 187]. The subject of thin film stability and draining of films is a separate line of research with the ultimate goal to understand foam and emulsion stability. Various papers on the relevance of the Plateau-Marangoni-Gibbs effect in this field have been published [188, 189, 190].

In packed columns, mass transfer was studied by Moens [191, 192], van der Klooster [140, 193], Patberg et al. [194] and later by Dijkstra [195]. Moens carried out distillations in packed columns and used the stabilisation index (see formula (7) later) to characterise the experiments. He constructed experimental graphs of the number of transfer units versus the stabilisation index and concluded that in positive systems the number of transfer units increases with increasing driving force. On the other hand, this dependence was slightly negative for negative systems. Van der Klooster and Patberg et al. also showed experimentally that the Marangoni effect is responsible for increased mass transfer during desorption in packed columns, provided the packing particles and the liquid load are relatively small. This is in accordance with predictions of Moens for the importance of scale. In general, the enhancement of mass transfer was found to be due to the influence of the Marangoni effect on both interfacial area and mass transfer coefficient.

The increased wetting of the packing by the Marangoni effect was described theoretically in the papers of Patberg et al. and Dijkstra on the creeping film phenomenon. Dijkstra constructed a model of a climbing film, consisting of three distinct areas. The increase in mass transfer due to creeping film was discussed qualitatively and Dijkstra theoretically demonstrated it to be proportional to the parameter Q^* and the Biot number.

$$Q^* = \left(-\frac{\partial \gamma}{\partial c} c_0 \right)^{0.6} (\mu D)^{-0.4} (\rho g)^{-0.2} \tag{4}$$

A hydrodynamic stability analysis of falling liquid films was performed by Wang, Ludviksson and Lightfoot, both for thermal [196] and solutal induced surface tension gradients [197]. In their last study, some of the experiments described by Zuiderweg and Harmens were qualitatively confirmed (formation of rivulets).

Semkov and Kolev analysed two approaches for correlating the effect of interfacial turbulence (Marangoni effect) in gas-liquid contactors, with the emphasis on finding relations valid for packed columns [36]. In literature, they found several parameters that are used to quantify the surface tension gradient effects. Apart from the definition of the Marangoni number presented in equation (2), several other definitions were found, as well as the so-called stabilisation index M.

$$Ma = \frac{\left(-\frac{\partial \gamma}{\partial c} \right) c_0 H}{\mu D} \tag{5}$$

$$Ma = \frac{\Delta \gamma}{k_L^* \mu} \tag{6}$$

$$M = \frac{d\gamma}{dx} (x - x_i) \tag{7}$$

In these equations, $\Delta\gamma$ is the surface tension difference between the values associated with the interface concentration and the bulk concentration, x the mole fraction, k_L^* the mass

transfer coefficient in the absence of interfacial turbulence and the subscript i refers to the gas-liquid interface. To express the mass transfer increase, usually the enhancement factor ϕ is introduced. Semkov and Kolev found two ways in which ϕ was correlated.

$$\phi = \frac{k_L}{k_L^*} \tag{8}$$

$$\phi - 1 = K\,Ma \tag{9}$$

$$\phi = \left(\frac{Ma}{Ma_C}\right)^n \tag{10}$$

In these equations, K and n are correlation parameters (K depends on the Biot number). Ma_c is the critical Marangoni number (depending on the Biot number) and represents the lower limit of mass transfer enhancement. Equation (10) is valid up to a limit (ϕ_∞), above which the exponent n vanishes.

Semkov and Kolev argue that the method represented by equation (9) is less correct as K is found to depend on Ma, or in other words, ϕ is not directly proportional to Ma. They have more objections to this method, proposed by Grymzin et. al. [198], and prefer the method represented by equations (6) and (10). They also correlate data to obtain expressions for Ma_c and n as a function of Biot number and use these expressions to model the Marangoni effect in packed columns [199]. However, their expressions are based on only one reference, and the modelling results do not prove the accuracy of their correlations. Furthermore, as Golovin [200] later shows, the data on which Semkov and Kolev base their relationships is quantitatively wrong. Finally, the correlations used by Semkov and Kolev have been deduced from experimental results for wetted wall columns, not for packed columns. The correlations used by the authors ignore the influence of the Marangoni effect on the interfacial area.

In a recent text book on packed columns by Billet [201], engineering calculations for the design of packed columns are presented. The liquid side mass transfer is calculated from the penetration theory. The interfacial area is determined from empirical relations. A correction for the Marangoni effect is only made for negative systems, in which case the interfacial area (a_{neg}) is smaller than the interfacial area (a) computed by an empirical relation. (Also Martin and Perez found a dependence of the mass transfer on Marangoni convection only in negative systems, albeit only qualitatively [202].)

$$\frac{a_{neg}}{a} = \left(1 - 2.4 \cdot 10^{-4} |Ma|^{0.5}\right) \tag{11}$$

$$Ma = \frac{\left(\frac{d\gamma}{dx}\right)\Delta x}{\mu\, D\, a_p} \tag{12}$$

In these equations, x is a mole fraction in the liquid, and Δx the difference in composition between the interface and the bulk, a quantity for which another empirical relation is provided.

Furthermore, a_p is the total surface area per unit packed volume. No references for this equation are provided, and neither are relations for the influence of the Marangoni effect on the mass transfer coefficient (k_L). Although this might already be incorporated in the numerous empirical relationships, as these represent averages of experiments with and without the Marangoni effect, it indicates that in industrial practice this aspect is usually considered negligible. This can be related to the large size of the packing and large liquid loads, as argued by Moens and Patberg. Also, Zuiderweg and Yanagi argue that in commercial scale packing, the effect of maldistribution might completely overshadow a Marangoni effect [203]. An aspect which was not discussed by Billet and Zuiderweg, is the possibility that a positive system can partly correct maldistribution of the liquid on the packing.

Most of the research on the influence of Marangoni convection on mass transfer in gas-liquid systems was directed towards its influence on the interfacial area. Considerably less effort was directed to the establishment of its influence on the mass transfer coefficient. There are several reasons for this. Firstly, the influence on the interfacial area is usually much larger than the influence on the mass transfer coefficient. As is evident from the text book of Billet [201], the influence of the Marangoni effect on the mass transfer coefficient is not taken into account. Moreover, a little pollution in a packed column easily destroys the flows that increase the mass transfer coefficient, but it does not so easily destroy the film-stabilising action of the Marangoni effect.

Nevertheless, for a complete understanding of the influence of the Marangoni effect, it is necessary to study both the influence on k_L as well as the influence on a, in order to be able to make a rigorous separation between them. Furthermore, knowledge on flows generated by the Marangoni effect could also be used for heat transfer applications, microgravity applications, liquid-liquid mass transfer and reaction engineering.

Experiments on the influence of Marangoni convection on the mass transfer coefficient were already performed by Linde and co-workers [204, 205, 206]. In the first two papers cited, they study the transfer of sodium-alkylsulfates between water and iso-amylol in both directions, with and without forced convection. In the last paper, a comparison is made between mass transfer and heat transfer in a system in which the instability is caused by a solutal effect. Although the mass transfer is strongly enhanced with respect to the case of pure diffusion, heat transfer is not. This is caused by the large value of the Lewis number.

In 1970, Clark and King presented a mass transfer study on the desorption of pentane, cyclopentane, diethyl ether and carbon disulfide from tridecane in a rectangular duct [207]. Apart from the case of desorption of carbon disulfide, and especially in the case of diethyl ether, a substantial enhancement of mass transfer was found above a critical solutal Marangoni number. In the case of diethyl ether, the mass transfer resistance in the liquid phase was so much reduced by the interfacial turbulence at higher driving forces, that the mass transfer was almost only determined by the gas phase mass transfer resistance. Data plotted according to formulas (6) and (10) revealed an exponent n = 0.25 at a small ratio of Marangoni number and critical Marangoni number. The liquid layer used in these experiment was 1.3 cm, and apart

from interfacial instabilities, also Rayleigh instabilities could have played a role in some of the experiments described, as was discussed theoretically.

Brian, Vivian and Mayr published an excellent basic paper on the desorption of diethyl ether, acetone, triethylamine and chloromethane from water in short wetted wall columns [208]. In order to measure the liquid and gas side mass transfer coefficient, two tracer components were used. Desorption of propene was used to measure the liquid side mass transfer, and water evaporation to measure the gas side mass transfer. Propene does not affect the surface tension appreciably and its solubility in water is low, making it a suitable tracer. The evaporation of water from dilute solutions is determined by the gas phase mass transfer, and its effect on the surface tension is minor compared to the effect of desorption of the surface active solutes. In the desorption experiments, only the liquid phase mass transfer coefficient was enlarged by the Marangoni effect, up to a factor of 3.6. The gas phase mass transfer coefficient was not influenced. Of the four solutes used in the study, only chloromethane did not cause a detectable Marangoni effect.

The results of Brian et al. could be correlated according to the method constituted by equations (6) and (10). The critical Marangoni number was found to depend on the Biot number, as predicted by Pearson [35], but the absolute values of the critical Marangoni number were orders of magnitude larger than predicted theoretically. In subsequent theoretical studies, Brian tried to obtain a better prediction of the critical Marangoni number by improving Pearson's analysis by incorporating Gibbs absorption and a non linear concentration profile as the undisturbed state [70, 71]. Although a large improvement resulted, the critical Marangoni number proved to be difficult to predict. The residual discrepancy between experimentally found critical Marangoni numbers and the ones predicted by Brian et al. is probably partly a result of the presence of traces of surface active pollutants.

Experiments were also performed in a pool column, which is characterised by its fixed interfacial area. Both Ellis and Biddulph [209] and Moens [210] found variations of mass transfer which could be attributed to the Marangoni effect. Moens concluded that a macroscopic effect was responsible for variations in mass transfer. This effect was a result of the fact that the liquid flowing into the pool had a different composition than the liquid in the pool. He considered the effect of microconvection to be of minor importance.

Desorption of diethyl ether and acetone from water in wetted wall columns was studied by van der Klooster [140]. For diethyl ether desorption the effective mass transfer coefficient was found to be considerably larger than theoretically predicted. Furthermore, the effective mass transfer coefficient was a function of the Marangoni number defined by equation (6). For acetone desorption only a minor enhancement was found with respect to theoretical predictions. No experimental comparison was made with mass transfer under neutral conditions, however. The differences between acetone and diethyl ether are a result of the different Biot numbers (in the diethyl ether desorption system the resistance to mass transfer is located primarily in the liquid phase while for the acetone desorption system the resistance is primarily located in the gas phase). A study with a Laser-Doppler-velocimeter revealed velocities in the film normal to the interface for the diethyl ether desorption system. The results were inconclusive, however.

Imaishi et al. performed experiments in a stirred gas-liquid contactor, wetted wall columns and liquid jets [211, 212]. An increased mass transfer rate in such a system can only be attributed to an increased mass transfer coefficient, not to increased interfacial area. Absorption and desorption of various components in and from aqueous solutions and the simultaneous desorption of oxygen was monitored. In wetted wall columns and liquid jets enhancement of the mass transfer coefficient according to equations (6) and (10) was found [212], the coefficient n being equal to 0.4. Golovin later demonstrated that the coefficient was wrongly calculated and should actually be 0.68 [200]. (This recalculation also has serious implications for the empirical relationship for n derived by Semkov and Kolev [36], as this relationship was based on the data by Imaishi et al..) Imaishi et al. were able to correlate the critical Marangoni number with the Biot number, including the results of Brian et al. [208]. The most significant contribution of Imaishi et al., compared to the paper of Brian et al., was the use of wetted wall columns and liquid jets of variable length. In this way the dependence on the contact time could be investigated. The same authors also studied mass transfer in a turbulent gas-liquid contactor (modified Lewis cell). Also in such a cell, desorption of acetone and methanol enhances the liquid side mass transfer coefficient of oxygen. Adsorption reduces the mass transfer coefficient. These effects could be explained by arguing that the interfacial turbulence respectively promoted and inhibited eddies generated by the agitation of the liquid [211].

Hirata et al. performed a theoretical study on the influence of a macroscopic Marangoni effect on heat and mass transfer in a system of two co-current semi-infinite phases [213]. A constant surface tension gradient was applied and the influence of the surface tension gradient on Nusselt numbers was studied. Basically, for positive systems, a relationship similar to equation (10) was found, n being equal to 1/3. However, no coupling between concentration and temperature fields and surface tension was made and the velocity normal to the interface was neglected, which makes the application of their study to real mass transfer systems quite difficult.

Golovin [200] developed a semi-empirical model to account qualitatively for the effect of the Marangoni number on the liquid side mass transfer coefficient. (Similar models can be found in the review and the references in it by Rabinovich [139] on modelling of mass transfer during interfacial turbulence.) In literature, Golovin found two types of relations: linear Sherwood-Marangoni relationships and power relationships as represented by equations (6) and (10). To account for these different dependencies, Golovin distinguished between chaotic cells and regular convective cells. The model he developed showed that for chaotic cells the Sherwood number depends linearly on the Marangoni number, and that for regular cells the Sherwood number is proportional to the cubic root of the Marangoni number, provided the Marangoni number is larger than the critical Marangoni number. Golovin argued that the different values of n (equation (10)) found by different authors reflect different types of mass transfer equipment. With forced convection and in wetted wall columns with large Reynolds numbers, n is closer to 1, while in wetted wall columns with small Reynolds number n is closer to 1/3. The model of Golovin seems to be the only explanation for the different values of n found in literature. This model is discussed in more detail in chapter 4.

Although correlations of the type represented by formula (10) are proposed both for wetted wall columns and packed columns, it should be emphasised that the mechanism for the enhancement of mass transfer can be quite different in both cases. For packed columns, the increase (or decrease) of interfacial area provoked by the Marangoni effect is not properly taken into account when equations derived for constant interfacial area are applied. Dijkstra made a first attempt to account for the effects of enlarged surface area and microconvection separately [214].

The influence of the Marangoni effect on the mass transfer coefficient in a negative system was only studied by Ellis and Biddulph, who found oscillatory rippling in absorption of acetone and methanol in water and argued that these ripples might influence the mass transfer coefficient [215]. The oscillatory movements are in agreement with the criteria of Sternling and Scriven.

Lu et al. published a series of papers on artificially induced Marangoni convection in a gas liquid system [27, 28, 29], based on a previous study by Ruckenstein et al. [26]. They studied the absorption of CO_2 in water while contacting the interface with a small stream of a liquid with low surface tension (for example an aqueous solution of an alcohol). The stream of liquid represented a surface tension sink and provoked Marangoni convection, which enhanced the absorption. In their first paper [27], a Sherwood-Marangoni relationship was found of the type represented by formula (10), the exponent being 0.35. This is in agreement with the theory of Golovin [200], who predicts an exponent of 0.33 for systems with regular roll cells. The system of Lu et al. falls into this category as the roll cells formed are induced by a macroscopic effect and constantly maintained, i.e. the form of the roll cell does not depend on time once the roll cells are formed. Lu et al.'s later papers detailed the influence of various components and surfactants used for the creation of the surface tension sink.

Warmuzinksi and co-workers have derived equations for the enhancement of mass transfer due to Marangoni convection during the absorption of CO_2 into aqueous monoethanolamine. A review of their work has recently appeared [84]. A relation of the type represented by equation (10) was found to be valid for a wide range of experiments; n being equal to 0.26. Rabinovich et al. also studied the enhancement of mass transfer by chemical reaction theoretically, and derived an expression for the enhanced Sherwood number as a function of various physical parameters [85].

In chapter 4 of this thesis, some of the results from literature presented above concerning the enhancement of mass transfer in gas-liquid systems are compared to results obtained from modelling the Marangoni convection in V-shaped containers (chapter 3).

Liquid-liquid systems

Apart from research on liquid-gas systems, extensive research has been done on the influence of the Marangoni effect on mass transfer in liquid-liquid systems (extraction). By the

mechanism of film (de-)stabilisation, coalescence phenomena are influenced, and surface tension gradients can determine droplet size and therefore the size of the interfacial area [216, 217]. In certain systems, these considerations can determine which phase should be preferentially the dispersed, and which the continuous phase.

Intensification of mass transfer in liquid-liquid systems as a result of interfacial instabilities has been experimentally proven by several authors [47, 50, 168, 218, 219, 220]. Maroudas and Sawistowski found that interfacial turbulence resulting from the transfer of one solute could enhance the mass transfer of another solute [47]. Berg and Haselberger observed mass transfer rates across horizontal liquid-liquid boundaries [168]. They discovered that the way the density normal to the interface was distributed significantly influenced mass transfer rates. Unstable density gradients as a result of mass transfer promoted interfacial turbulence and mass transfer rates. The influence of density gradients on mass transfer, however, is only significant in the thick liquid layers Berg and Haselberger used for this study (several cm).

Ostrovsky and Ostrovsky studied the dissolution of drops in binary liquid-liquid systems [221]. They demonstrated theoretically and experimentally that solutal Marangoni effects can also play a role in binary systems. Solutal effects can occur as a result of varying dynamic surface tension, rather than a result of varying static surface tension, an argument first provided by Austin, Ying and Sawistowski [51, 220]. Previously, Ortiz and Sawistowski had explained interfacial instability in binary systems in terms of temperature gradients associated with mass transfer [**Fout! Bladwijzer niet gedefinieerd.**, 78]. Ostrovsky and Ostrovsky found the intensity of drop pulsation in such systems and the dissolution of drops to depend on the driving force. Both Rayleigh and Marangoni effects were found to play a role. Unfortunately, in the paper of Ostrovsky and Ostrovsky no clear indication was given as to what extent the Marangoni effects were caused by thermal or solutal effects.

Thornton et al. observed surface renewal due to the Marangoni effect during droplet formation at a nozzle. For this a photochromic tracer technique was employed. The Marangoni effect clearly increased the surface renewal rate. As a matter of fact, no surface renewal was observed in equilibrated droplets at all. The surface renewal rate was observed to increase with the driving force for mass transfer [222]. In a subsequent study by the same authors, the mass transfer coefficient of acetone from toluene into water was measured, water being the dispersed system [223]. The larger the driving force was, the larger the mass transfer coefficient. The mass transfer coefficient also proved to depend on time, although the experimental system provided for a constant driving force. Obviously, the age of the interface also played a role. No sufficient explanation was provided, however.

Ruckenstein discussed qualitatively the influence of the Marangoni effect on the mass transfer from a bubble in a continuous liquid [224]. Due to mass transfer, solute concentration gradients can occur which can enhance or reduce internal circulation velocities. When a drop falls in another liquid, an internal flow in the droplet accelerates the settling velocity compared to the settling velocity of a rigid sphere. When, however, surface active substances are present, these are forced to the wake side of the droplet by friction with the external fluid. The resulting surface tension gradient acts as an opposing force to the external friction, making the droplet more or less rigid. This process decreases mass transfer rates to or from the droplet.

Batey et al. provided for a (patented) method to account for the effect of Marangoni convection on coalescence phenomena in extraction columns [217]. The method, which was developed for extraction equipment in nuclear industry, first requires a set of experiments relating the dispersed phase hold-up to the dispersed and continuous phase velocities. Plotted in the right way, a single empirical constant can then easily be obtained, with which the influence of the Marangoni effect on coalescence can be characterised uniquely. Strangely, their patent only mentions the situation in which coalescence is enhanced by the Marangoni effect, and no effect of solute concentration or driving force is discussed.

A semi-empirical model for the enhancement of mass transfer to a single moving drop was proposed by Golovin et al. [219], along the same lines as described earlier by Golovin [200]. Experiments were performed to estimate the empirical constants in the model. Relations for mass transfer in multi-component liquid-liquid systems in the presence of Marangoni convection have been derived and checked by Ermakov et al. [225]. The transfer of a microcomponent (low concentration; phenol) with the simultaneous transfer of a macrocomponent (larger concentration; propanoic acid) between water and tetrachloroethene was measured. A strong interaction was observed, the interaction, at least in part, being a result of interfacial turbulence. The mass transfer coefficient increased linearly with the concentration difference between bulk and interface, provided a critical concentration difference was exceeded.

A book treating many aspects of the Marangoni effect in liquid-liquid extraction has recently been published [187].

Influence on heat transfer

Apart from increasing mass transfer rates, solutal Marangoni convection can also increase heat transfer rates [76, 81, 206]. At the University of Eindhoven in the Netherlands, a research program has been set up to study the Marangoni effect in heat transfer equipment [226]. In condensation and boiling equipment, thermocapillary motion can increase heat transfer rates [227]. However, a solutal Marangoni effect could be used to further enhance heat transfer, by adding traces of surface tension lowering solutes to either vapour or liquid. In a recent paper by Morrison and Deans, a short review on this subject and data on steam condensation in the presence of ammonia were presented [228]. Up to a 13 % increase in heat transfer was found for a limited concentration range, which could be attributed to a 32 % increase in condensation heat transfer due to the Marangoni effect moderated by a decrease in heat transfer in the vapour film caused by the additional component.

The occurrence of Marangoni effects in LiBr absorbers has been the subject of various studies [75, 76, 229]. In absorption refrigerators, steam is absorbed in solutions of LiBr in water. If octanol is added to the LiBr solution, Marangoni instabilities increase the heat transfer. Absorption refrigerators are widely used for air conditioning, and an increase in heat transfer can make this equipment more compact.

Nemchinsky presented theoretical and numerical results on the increase of heat transfer in a liquid droplet during arc welding [230]. During the melting of the metal electrode, macroscopic thermocapillary motions occur in the metal droplet, and heat transfer rates can exceed thermal conduction heat transfer rates tenfold.

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